

CLAIMS:

1. A below 193 nm VUV transmitting glass photomask substrate for photolithography at wavelengths of about 157 nm comprising high purity silicon oxyfluoride glass with an OH content below 50 ppm by weight, hydrogen content below 1×10^{17} molecules/cm³, and fluorine content in the range of 0.1 to 0.4 weight percent.
2. A VUV photomask substrate according to claim 1 wherein the glass has a Cl content below 5 ppm.
3. A VUV photomask substrate according to claim 1 wherein the molecular hydrogen content is below 3×10^{16} molecules/cm³.
4. A VUV photomask substrate according to claim 1 wherein the fused silica is characterized by having no detectable molecular hydrogen content.
5. A VUV photomask substrate according to claim 1 wherein the OH content is below 10 ppm by weight.
6. A VUV photomask substrate according to claim 1 wherein the OH content is below 1 ppm by weight.
7. A VUV photomask substrate according to claim 1 further characterized by having internal transmittance of at least 89 %/cm at 157 nm wavelength region.
8. A VUV photomask substrate according to claim 7 wherein the measured transmittance is at least 79 % through a thickness of the photomask substrate.
9. A VUV photomask substrate according to claim 8, wherein the thickness is about 6 mm.

10. A VUV photomask substrate according to claim 1, further characterized by being essentially free of chlorine.

5 11. A VUV photomask substrate according to claim 1, said silicon oxyfluoride glass

comprised of Si, O and F and is essentially free of OH, Cl and H₂.

12. A VUV photomask substrate according to claim 1, wherein said glass has a low H₂ content such that less than 10¹⁸ H₂ molecules/m² are released when heated under a vacuum to about 1000°C.

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13. A VUV photomask substrate according to claim 1, wherein said photomask substrate is free of an absorption peak at 4,100 cm⁻¹.

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14. A process of making a VUV transmitting glass having high resistance to optical damage to excimer laser radiation in the 157 nm wavelength region, said process comprising the steps of:

providing particles of SiO₂;

dehydrating the particles;

20 fluorine doping and consolidating the particles to form a dry, non-porous monolithic body of transparent fused silicon oxyfluoride glass with a fluorine content less than 0.5 weight percent.

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15. A process according to claim 14, wherein the particles are reacted with a fluorine-containing gas such that the amount of fluorine incorporated into the glass resulting from consolidation is in the range of 0.1 to 0.4 weight percent.

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16. A process according to claim 15 wherein the fluorine-containing gas is selected from the group consisting of CF₄, SiF₄, F₂, SF₆, C₂F₆, C₃F₈ and mixtures thereof.

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17. A silicon oxyfluoride glass suitable for use in the 157 nm wavelength region, said glass having essentially no OH groups, 0.1 to 0.4 weight % fluorine, and less than 5x10¹⁶ molecules/cm³ of molecular hydrogen.

5 18. A lithography glass comprising a silicon oxyfluoride glass, said silicon oxyfluoride glass having an OH content less than 5 ppm by weight, a Cl content less than 5 ppm by weight, a H₂ content less than 1×10^{17} molecules/cm³, and a fluorine content of 0.1 to 0.4 weight %, said glass having a 157 nm internal transmission of at least 85%/cm.

10 19. A lithography glass as claimed in claim 18, wherein said glass has a 157 nm transmission loss < 1% after exposure to a 157 nm laser for 60 million pulses at 0.1 mJ/cm²-pulse.

15 20. A lithography glass as claimed in claim 18, wherein said glass has a resistance to 157.6 nm induced absorption.

20 21. A lithography glass as claimed in claim 18, wherein said fluorine content inhibits 165 nm absorption oxygen-deficient centers.

25 22. A lithography glass as claimed in claim 18, wherein said glass has a 165 nm absorption less than 0.4 (absorption units/5mm) after exposure to a 157 nm laser for 41.5 million pulses at 2mJ/cm² pulse.

30 23. A lithography glass as claimed in claim 22, said 165 nm absorption less than 0.3 (absorption units/5mm) after a 157 nm laser for 41.5 million pulses at 2mJ/cm² pulse.

24. A glass as claimed in claim 23 wherein said 165 nm absorption is less than 0.2 (absorption units/5 mm).

25. A glass as claimed in claim 18 wherein said Cl content is less than 1 ppm and said OH content is less than 1 ppm.

26. A glass as claimed in claim 18 wherein said glass consists essentially of Si, O, and F.

27. A VUV transmitting photomask comprised of the glass as claimed in claim 18.

28. A VUV phase shifting photomask comprised of the glass as claimed in claim 18.

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29. A photomask of the glass as claimed in claim 18, said photomask having a resistance to laser induced oxygen deficient centers.

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30. A glass as claimed in claim 18 wherein said glass is essentially free of metal to metal Si-Si bonds.

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31. A photomask as claimed in claim 30 wherein said glass is free of a 165 nm absorbing center and has an internal transmission at 165 nm of at least 85%/cm.

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32. A VUV pattern printing method, said method comprising:
providing a below 164 nm radiation source for producing VUV photons,
providing a silicon oxyfluoride glass having less than 5 ppm by weight OH, less than 5 ppm by weight Cl and a < 0.5 weight percent fluorine content, and 157 nm and 165 nm measured transmission of at least 75%/5mm,
transmitting said VUV photons through said silicon oxyfluoride glass,
forming a pattern with said VUV photons,
and projecting said pattern onto a VUV radiation sensitive printing medium to form a printed lithography pattern.

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33. A method as claimed in claim 32 wherein providing a silicon oxyfluoride glass comprises lowering the VUV cut off wavelength of the glass by providing an SiO_2 glass forming precursor, and doping with a F content to provide a silicon oxyfluoride glass with a 50% transmission VUV cut off wavelength below 160 nm and a 165 nm absorption less than 0.4 (absorption units/5mm) after exposure to a 157 nm laser for 30 41.5 million pulses at $2\text{mJ}/\text{cm}^2$ -pulse.

34. A method as claimed in claim 32 wherein said silicon oxyfluoride glass consists essentially of Si, O, and F and is essentially free of Si-Si bonds.

5 35. A VUV transmitting silicon oxyfluoride glass having an OH content less than 1 ppm by weight, a Cl content less than 1 ppm by weight, a H₂ content less than 1×10^{17} molecules/cm³, a fluorine content of 0.1 to 0.4 weight %, said glass having a 165 nm absorption less than 0.4 (absorption units/5mm) after exposure to a 157 nm laser for 41.5 million pulses at 2mJ/cm²-pulse.

10 36. A VUV transmitting silicon oxyfluoride glass having an OH content less than 5 ppm by weight, a Cl content less than 5 ppm by weight, a H₂ content less than 1×10^{17} molecules/cm³, a fluorine content of at least 0.1 weight %, said glass consisting essentially of Si, O and F and having a 165 nm absorption less than 0.4 (absorption units/5mm) after exposure to a 157 nm laser for 41.5 million pulses at 2mJ/cm²-pulse.